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INFORMATION  
ON THE  
PATENT ACT  
R.S.C. 1985, c. P-43

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(22)	1993/12/01
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(19) (CA) APPLICATION FOR CANADIAN PATENT (12)

(54) Composition and Methods for Inhibiting the Corrosion of  
Low Carbon Steel in Aqueous Systems

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(57) 18 Claims

Notice: This application is as filed and may therefore contain an  
incomplete specification.



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ABSTRACT

Methods and compositions are provided for inhibiting the corrosion of low carbon steel in contact with an aqueous system. The compositions comprise a combination of a silicon compound containing a hydrolyzable group attached to an Si-O grouping and a complex fluoro acid.

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COMPOSITION AND METHOD FOR INHIBITING THE CORROSION  
OF LOW CARBON STEEL IN AQUEOUS MEDIUMS

FIELD OF THE INVENTION

5       The present invention relates to compositions and  
methods of providing a durable, long lasting chemically resistant  
corrosion inhibiting film on the surface of low carbon steel.

BACKGROUND OF THE INVENTION

10       In aqueous systems, particularly industrial aqueous  
systems, metallic parts need to be protected from corrosion and  
corrosion by-products. The metallic parts of these systems which  
are exposed to the aqueous fluid could include heat exchangers,  
boilers, pipes, engine jackets, and the like. The cooling fluid  
contains aggressive ions which are often corrosive towards these  
metal parts. The introduction of oxidizing substances for bio-  
15       logical control will increase the aggressiveness of the cooling  
fluid toward the metal parts. Corrosion inhibitors are generally  
added to the aqueous system to prevent metal loss, and pitting.



The use of conventional corrosion inhibitors have certain disadvantages. Chromates, are efficacious as corrosion inhibitors, but are known to be very toxic. Zinc has solubility limitations and has also been shown to be toxic to aquatic life. Phosphates and organophosphonates can lead to scale and deposition unless effective deposit control agents are added and well controlled. In addition, phosphorus containing compounds, while not directly toxic to aquatic life, can promote environmental problems such as eutrophication of surface waters. There currently exists a great need for non-chromate, non-phosphorus corrosion inhibiting treatments.

#### SUMMARY OF THE INVENTION

The invention relates to compositions and methods of providing a durable, long lasting chemically resistant corrosion inhibiting film on the surface of low carbon steel.

These aqueous solutions are dilute and are carried to the LCS surface via the aqueous media and react with the surface in contact with the aqueous media. Unlike a traditional conversion coating process, the aqueous solution is never dried and a second coating, such as paint, is not necessarily required.

## DESCRIPTION OF THE RELATED ART

U.S. 4,744,950, Hollander, teaches methods for inhibiting copper corrosion in cooling water systems. Alkyl benzotriazole compounds provide a lasting film on the copper surfaces in contact with the aggressive waters of an open cooling water system.

U.S. 4,303,568, May et al., teaches methods and compositions for inhibiting the corrosion of ferrous metals in contact with aqueous systems. A passive oxide film can be formed on the ferrous surfaces by adding a composition which comprises a polymer of acrylic moieties and hydroxylated lower alkyl acrylate moieties, and a water soluble orthophosphate.

## DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to compositions and methods of providing a durable, long lasting chemically resistant corrosion inhibiting film on the surface of low carbon steels comprising adding to said steels an effective amount of an aqueous solution of a silicon compound containing a hydrolyzable group attached to a Si-O grouping and complex fluoro acid.

It has been discovered that low concentrations of silicon compounds and fluorozirconic acid form a tenacious film or coating on the surfaces of low carbon steels. The formation of

this protective coating or film utilizing silicon compounds needs no drying or direct application steps. This corrosion inhibition is achieved with no other corrosion inhibitor present.

5           The silicon compounds useful in this invention can be selected from silicon compounds containing Si-O bonds that are attached to a group that is easily hydrolyzed such as an alkoxy. Inorganic silicates also have Si-O bonds with easily hydrolyzed inorganic salts attached. Representative compounds include  
10 N-( $\beta$ -aminoethyl) -  $\gamma$ -aminopropyltrimethoxysilane which is commercially available from Dow Chemical Corporation as Z-6020, methyltriacetoxysilane and -aminopropyltriethoxysilane, both available from Huls, and sodium silicate. The inventors anticipate that any compound containing a hydrolyzable group,  
15 attached to a Si-O grouping will also be effective in the instant invention.

          The composition can be applied to the low carbon steel by a variety of methods. The composition can be applied by immersion of the low carbon steel or by spraying onto the steel  
20 surface. However, sufficient contact time between the composition and the steel surface must be made for the treatment to be effective.

          The composition is best applied to the steel to be treated as an aqueous solution. It has been found that amounts  
25 as low as 10 parts per million parts of each component will form



a tenacious film on the low carbon steel. As much as 1000 parts per million of each component can be effectively employed to create the corrosion inhibiting film. Preferably, these amounts range from about 25 to about 500 parts per million

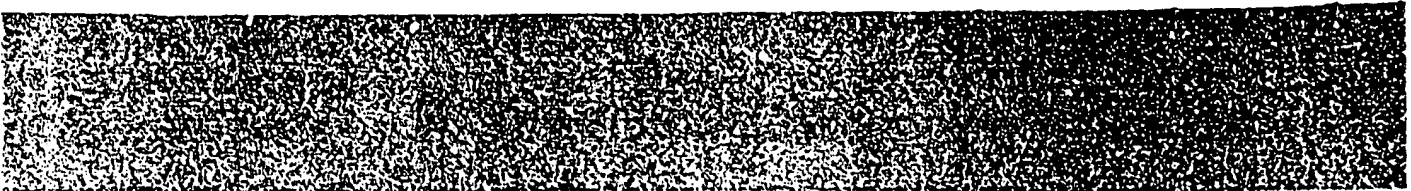
5           It is anticipated that the compositions and methods of the present invention would be effective for corrosion inhibition in cooling applications. The present invention also would eliminate the use of chromium for various treatments and thus is environmentally safer to use.

10           Although the compositions of the present invention inhibit corrosion without other corrosion inhibitors present, they may also be used in conjunction with other additives to inhibit corrosion.

15           In order to more clearly illustrate this invention, the data set forth below are developed. The following examples are included as being illustrations of the invention and should not be construed as limiting the scope thereof.

#### Examples

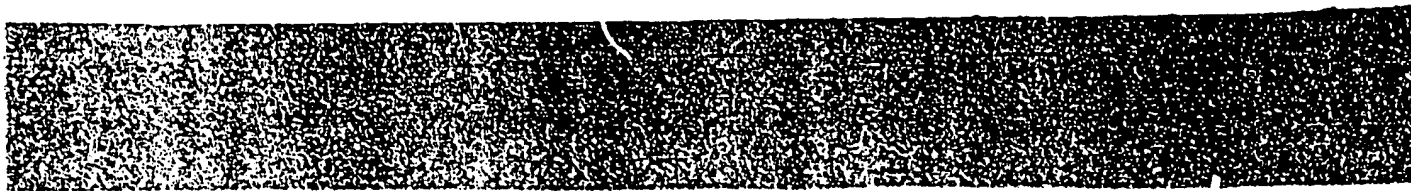
20           Testing was conducted in a beaker corrosion test apparatus (BCTA) which employed linear polarization to measure the corrosion of low carbon steel in mils per year (mpy).



Testing was performed in the BCTA in a moderate hardness water at pH 8.4 with the following conditions:

5	250 ppm Ca (as $\text{CaCO}_3$ )	200 ppm $\text{SO}_4$
	125 ppm Mg (as $\text{CaCO}_3$ )	12 ppm $\text{SiO}_2$
	300 ppm Cl	166 ppm Na
	80 ppm M alkalinity (as $\text{CaCO}_3$ )	

All test waters contained 1 ppm of hydroxyethylidene diphosphonic acid (HEDP) and 5 ppm of acrylic acid/allyl hydroxy propyl sulfonate copolymer for deposition control. These test results are presented in Table I.



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TABLE 1

1 Hour Contact Time

	Silicon Compound (ppm)	H <sub>2</sub> ZrF <sub>6</sub> (ppm)	Passivation pH	Corrosion Rate (mpy)*
5	-----	---	---	56.1
	2781 <sup>1</sup> (100)	50	3.27	2.35
	2775 <sup>2</sup> (100)	50	4.37	1.44
	2775 (50)	50	3.56	2.07
10	2775 (25)	25	3.83	2.88
	MTAS <sup>3</sup> (25)	25	2.14	3.59
	2132 <sup>4</sup> (100)	50	3.70	41
	BKY <sup>5</sup> (100)	50	3.65	43

\* Averaged over 18 hour exposure to test solution.

- 15 1 vinyl-trimethoxysilane, available as Huls 2781  
 2 triminopolytrimethoxysilane, available as Huls 2775  
 3 methyltrimethoxysilane, available from Huls  
 4 polydimethylsilane-polyoxyalkylene, available as Masil 2132  
 from PPG Mazer  
 20 5 polyether modified dimethylpolysiloxane-copolymer,  
 available as BKY 301 from BKY Chemie.

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5        These results indicate the vastly improved differences  
between the inventive composition compared to the system which  
was not passivated. These results further indicate that the  
compositions of the instant invention prove effective at low  
dosages. Pretreatments 2132 and SKY proved ineffective as,  
although they are silicon compounds, they are stabilized silanes  
that possess ether bonding which makes them less easily  
hydrolyzable.

10        Other silicon compounds containing easily hydrolyzable  
groups were tested with fluorozirconic acid under the same test  
conditions. These results are presented in Table II.

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TABLE II

1 Hour Contact Time

5	Silicon Compound (ppm)	$H_2ZrF_6$ (ppm)	Passivation	Corrosion
			pH	Rate (mpy)*
	A (25)	25	2.80	0.45
	B (25)	50	3.86	2.78
	C (25)	25	3.5	2.1 (3.4)

\* Averaged over 18 hour exposure to test solution

10 A is sodium 3 (trihydroxysilyl) - propylmethylphosphonate available as Q16083 from Dow Corning

B is sodium silicate R (ratio of  $Si-O_2:N_2O$ ) = 1

C is sodium silicate R = 3.22

15 The present inventors anticipate that all soluble silicate compounds including sodium, potassium and lithium silicates would also be effective in the present inventive composition.

20 Testing was also performed in a bench-top test unit (BTU). This allows for the testing of "cold" surfaces through the coupons of a bypass rack as well as simulated heat exchange surfaces. Pretreatment was carried out directly in the BTU for one hour at 120°F with 50 ppm  $H_2ZrF_6$  and 50 ppm of Dow's 2-6020 silane, designated N-( $\beta$ -aminoethyl) -  $\gamma$ -aminopropyl-trimethoxysilane. After pretreatment, the silane solution was replaced with a water of the following matrix:

400 ppm Ca (as CaCO<sub>3</sub>)      150 ppm Mg (as CaCO<sub>3</sub>)  
 51 ppm Si-O<sub>2</sub>      244 ppm Na  
 284 ppm Cl      470 ppm SO<sub>4</sub>  
 205 ppm M Alkalinity (as CaCO<sub>3</sub>)

- 5      1 ppm HEDP and 5 ppm acrylic acid/allyl hydroxy propyl sulfonate copolymer were present as deposition inhibitors.

The heater wattage was set at 308°F, resulting in a skin temperature of 130°F. The sump temperature was 120°F. Results of this testing are reported in Table III.

10

TABLE III

BTU Testing

		Corrosion Rate		
		Test 1	Test 2	Test 3
		<u>mpy</u>	<u>mpy</u>	<u>mpy</u>
15	Pretreated coupon (1 day)	11.5	10.4	
	Pretreated coupon (7 days)	6.2	2.1	2.0
20	Pretreated coupon (40 days)			0.8
	Non-pretreated coupon (1 day)	43		
25	Tube appearance	Clean Tube-out Day 7	Clean Tube-Out Day 16	Clean Tube-Out Day 40

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In all tests within two days the heat "transfer" tube developed the dark blue interference film. In Test 1 the tube was removed after 7 days, in Test 2 after 16 days, and in Test 3 after 40 days. In all tests, the heat exchange surface was clean with no indication of corrosion. The inventors anticipate that the localized heat on the surface of the tube actually enhances the tenacity of the film.

Comparative testing was performed against a known pre-treatment inhibitor utilizing the BCTA. Water conditions were the same as those in Tables I and II. These results are presented in Table IV.

TABLE IV

6 Hour Contact Time		ppm	Passivation pH	Corrosion Rate(mpy)*
15	Treatment			
	1) Zinc Phosphate Prefilm	800	4.26	40
	Ca (as $\text{CaCO}_3$ )	170		
	Mg (as $\text{CaCO}_3$ )	110		
	2) 2775	100	4.49	5.43
20	$\text{H}_2\text{ZrF}_5$	50		
	3) 2775	100	4.42	7.81
	$\text{H}_2\text{ZrF}_5$	50		

\* Averaged over 18 hour exposure to test solution

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These results indicate the relative superiority of the silicon compound fluorozirconic acid composition at inhibiting low carbon steel corrosion when compared to a known pretreating agent.

5 Table V presents results of testing in moderate hardness water with the same conditions as in Table I. These results indicate that although the acid will inhibit corrosion by itself, corrosion reduction is dramatically improved when the acid is used in conjunction with an appropriate silicon compound. Further, the optimum pH of the passivation solution should be in the acid range  
10 to achieve complete surface coverage of the film.

TABLE V

Moderate Hardness Water		ppm	Passivation pH	Corrosion Rate (mpy)*
Treatment				
15	1) $H_2ZrF_6$	25	2.54	3.17
	2) Silicate	25	3.5	2.1
		$H_2ZrF_6$		
	3) Silicate	25	5.6	42.6
		$H_2ZrF_6$		



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TABLE V (Cont'd)

Moderate Hardness Water		ppm	Passivation	Corrosion
<u>Treatment</u>			<u>pH</u>	<u>Rate(mpy)*</u>
5	4) 2775	50	6.98	61
	H <sub>2</sub> ZrF <sub>6</sub>	25		
	5) 2775	25	3.83	2.88
	H <sub>2</sub> ZrF <sub>6</sub>	25		

\* Averaged over 18 hour exposure to test solution

- 10 Table VI demonstrates that only complex fluoro acids are effective in the formation of the protective film on mild steel. The use of hydrofluoric acid (HF) does not promote film formation or offer protection to mild steel.

TABLE VI

15	Moderate Hardness Water			
	<u>Treatment</u>	<u>ppm</u>	<u>Passivation pH</u>	<u>Corrosion Rate(mpy)*</u>
	1) None	---	---	56
	2) 2775	100	5.0	5.5
20	H <sub>2</sub> ZrF <sub>6</sub>	50		

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TABLE VI (Cont'd)

Moderate Hardness Water		ppm	Passive pH	Corrosion Rate * mpy
Treatment				
5	3) 2775	100	4.3	18
	H <sub>2</sub> TiF <sub>6</sub>	50		
	4) Z-6020	25	3.	3.7
	H <sub>2</sub> ZrF <sub>6</sub>	25		
10	5) Z-6020	25	3.	84
	HF	25		

\* Averaged over 18 hour exposure to test solution

While this invention has been described with respect to particular embodiments thereof, it is apparent that numerous other forms and modifications of this invention will be obvious to those skilled in the art. The appended claims and this invention generally should be construed to cover all such obvious forms and modifications which are within the true spirit and scope of the present invention.

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THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A method of inhibiting the corrosion of low carbon steel surfaces in contact with an aqueous system comprising adding an effective amount of (a) a silicon compound containing a hydrolyzable group attached to a Si-O grouping and (b) a complex fluoro acid.  
5
2. The method as claimed in claim 1 wherein said silicon compound is triamino polytrimethoxy silane.
3. The method as claimed in claim 1 wherein said silicon compound is vinyl-trimethoxy silane.
4. The method as claimed in claim 1 wherein said silicon compound is N-( $\beta$ '-aminoethyl) -  $\gamma$  - aminopropyltri-methoxysilane.
5. The method as claimed in claim 1 wherein said fluoro acid is fluorozirconic acid.
6. The method as claimed in claim 1 wherein said fluoro acid is fluorotitanic acid.
7. The method as claimed in claim 1 wherein said silicon compound and said fluoro acid are added to the steel in a carrier solvent.

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8. The method as claimed in claim 7 wherein said solvent is water.

9. The method as claimed in claim 1 wherein said aqueous system is a cooling water system.

10. The method as claimed in claim 1 wherein said low carbon steel surfaces comprise the surfaces of a heat exchanger.

11. The method as claimed in claim 1 wherein said silicon compound and said fluoro acid are each added to said aqueous system in an amount ranging from about 10 parts to about 1000 parts per million parts aqueous system.

12. A low carbon steel corrosion inhibiting composition comprising a liquid carrier and dispersed or dissolved therein (a) a silicon compound containing a hydrolyzable group attached to a Si-O grouping and (b) a complex fluoro acid.

13. The composition as claimed in claim 12 wherein said silicon compound is triamino polytrimethoxy silane.

14. The composition as claimed in claim 12 wherein said silicon compound is vinyl trimethoxy silane.

15. The composition as claimed in claim 12 wherein said silicon compound is N-( $\beta$ -aminoethyl)- $\gamma$ -aminopropyltrimethoxy-silane.

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16. The composition as claimed in claim 12 wherein said fluoro acid is fluorozirconic acid.

17. The composition as claimed in claim 12 wherein said fluoro acid is fluorotitanic acid.

18. The composition as claimed in claim 12 wherein said liquid carrier is water.

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